

# PROCEEDINGS OF THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

## *The Aspherical Nucleus Theory applied to the Balmer Series of Hydrogen.*

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The purpose of the present paper is to apply the quantum theory of spectrum emission by atomic systems containing an *aspherical* nucleus, given in my recent paper,\* to the Balmer series of hydrogen. Although, in working out the general formulæ of the said theory, I have had in view chiefly the more complicated, non-hydrogenic, spectra as a possible field of its application, yet it has seemed worth while to compare also the aspherical nucleus formulæ with the Balmer spectrum of hydrogen, the more so, as recent measurements have revealed a notable deviation of at least the first six members of this series from the simple Balmer formula. The measurements alluded to were made by W. E. Curtis in 1914, and their newly revised results are tabulated in his paper of 1919,† for a copy of which accompanied by helpful explanations, I am indebted to Prof. Fowler.

1. It will be sufficiently general for the purpose in hand to assume an *axially symmetrical* nucleus of unknown asphericity (to be determined from the observations). Then the series will be given by the formulæ (28), (28.1),‡ with  $\kappa = 1$  (*i.e.*, nucleus charge =  $e$ ), with  $n' = 2$  written for the constant term, and  $n = 3, 4, 5$ , etc., for the members  $H_\alpha, H_\beta, H_\gamma$ , etc., of the series. Thus, if  $N$  be the Bohr value of the Rydberg constant, and if (retaining all other symbols of my quoted paper) we write for brevity

$$\sigma = \left( \frac{2Nch}{e^2} \right)^2 \cdot (A-B), \quad (1)$$

\* "Spectra of Atomic Systems containing a Complex (*i.e.*, Aspherical) Nucleus," 'Phil. Mag.,' vol. 39, pp. 46-66 (1920).

† W. E. Curtis, 'Roy. Soc. Proc.,' A, vol. 96, pp. 147-155.

‡ *Loc. cit.*, p. 62.

the frequency formula will be

$$\nu = \frac{N}{4} \left\{ 1 + \frac{4\sigma g'}{(2-n'_3)^6} \right\} - \frac{N}{n^2} \left\{ 1 + \frac{n^2 \sigma g}{(n-n_3)^6} \right\}, \quad (2)$$

where  $g = g(i, \epsilon)$  for the initial, and  $g'$  for the final orbit, are as on p. 55 (*loc. cit.*). It will be kept in mind that  $A-B$ ,\* and, therefore,  $\sigma$ , may be either positive or negative, according as the nucleus is "oblate" or "prolate" in the generalised sense of these words, as explained in the quoted paper. The variable number  $n$  is the sum of the three independent integers  $n_1, n_2, n_3$ , introduced through the quantum integrals, and, similarly,  $n' = n'_1 + n'_2 + n'_3$ , the quantised eccentricity  $\epsilon$  and inclination  $i$  of the electronic orbits, appearing in  $g(i', \epsilon)$ , being given by (21.3), *loc. cit.*

2. According to (2), every "member" or group of the series, such as  $H_\alpha (n=3)$ , will consist of many single lines or components. Let us call *main components* those lines in each group which correspond to the passage of the electron from a circular equatorial (initial) to a circular equatorial (final) orbit, *i.e.*, for  $i = \epsilon = 0$  and  $i' = \epsilon' = 0$ . This corresponds to  $n_2 = n_3 = 0$  and  $n'_2 = n'_3 = 0$ . Thus  $n = n_1$ ,  $n' = 2 = n'_1$ ,  $g = g' = 1$ , and the series of the main components will have (by 2) the frequencies

$$\nu = N \left\{ \left( \frac{1}{2^2} - \frac{1}{n^2} \right) + \sigma \left( \frac{1}{2^6} - \frac{1}{n^6} \right) \right\}, \quad (3)$$

where  $n = 3, 4$ , etc., for  $H_\alpha, H_\beta$ , etc.

In the absence of better knowledge, and in a first attempt, let us correlate these frequencies of the *main components* with those *measured by Curtis*, and let us see whether the two constants  $N$  and  $\sigma$  can be determined so as to represent his observations by formula (3) with sufficient accuracy. At a later opportunity, we may try, if need be, to improve this correlation of theory with observation.

Curtis has measured only the first six members of the Balmer series, and his vacuum wave-lengths, in  $\text{\AA}$ , with their probable errors in  $10^{-4} \text{\AA}$ ,† are

$H_\alpha (n=3).$	$H_\beta (4).$	$H_\gamma (5).$
6564.6022 $\pm$ 17	4862.6797 $\pm$ 10	4341.6830 $\pm$ 6
$H_\delta (6)$	$H_\epsilon (7)$	$H_\zeta (8)$
4102.8915 $\pm$ 13	3971.1940 $\pm$ 16	3890.1489 $\pm$ 11,

and the corresponding frequencies  $\nu$  are

$$15233.21_6 \quad 20564.79_3 \quad 23032.54_3 \quad 24373.05_5 \quad 25181.34_3 \quad 25705.95_7,$$

with probable errors which are at once derivable from those of the  $\lambda$ .

\*  $A, B$  are the (electrical) "moments of inertia" of the whole nucleus charge, as defined on p. 61, *loc. cit.* The dimensions of these constants,  $A, B$ , characterising the nucleus, are those of a squared length.

† *Loc. cit.*, pp. 148 and 151.

Let us determine  $N$  and  $\sigma$  by the method of least squares from *all six* observations, notwithstanding that the uncertainty of a coincidence between our "main" component and Curtis's observed "centre" is much greater in the case of the broad group  $H_\alpha$  than in the remaining ones. The resulting Gaussian normal equations are

$$\begin{aligned} 0.25557314_3 N + 0.018845437 N \sigma &= 28030.95_6, \\ 0.018845437 N + 0.001413238_8 N \sigma &= 2066.9451_9. \end{aligned}$$

Whence the required two constants become

$$\left. \begin{aligned} N &= 109678.0_8 \\ \sigma &= +9.007 \cdot 10^{-5} \end{aligned} \right\} \quad (4)$$

so that the hydrogen nucleus would be *oblate*.\* With these values of the coefficients formula (3) gives  $\lambda = 1/\nu$  which differ from Curtis's  $\lambda$ -values by the following amounts,  $\Delta\lambda = \lambda_{\text{calc.}} - \lambda_{\text{obs.}}$

$$\begin{array}{ccc} H_\alpha. & H_\beta. & H_\gamma. \\ 10^4 \cdot \Delta\lambda = +36 (\pm 17) & +2 (\pm 10) & -13 (\pm 6) \\ H_\delta. & H_\epsilon. & H_\zeta. \\ -10 (\pm 13) & -6 (\pm 16) & +3 (\pm 11) \text{ I.A.} \end{array}$$

The agreement for  $H_\beta$ ,  $H_\delta$ ,  $H_\epsilon$ ,  $H_\zeta$ , is complete, the differences being considerably smaller than Curtis's (bracketed) probable errors. For  $H_\alpha$  and  $H_\gamma$  the differences are about twice his probable errors; but even these are not unsatisfactory, being of different signs (+36 and -13), and the group  $H_\alpha$  being so broad that two or three thousandths of Å.U. can perhaps be thrown upon his fixing not our main component, but a slightly different place of the group. In fact, Paschen† quotes, for  $H_\alpha$ ,  $\lambda_{\text{air}} = 6562.797$ , which is by 0.004 greater than Curtis's value, and gives  $\lambda_{\text{vac}} = 6564.606$ , which agrees completely with our calculated  $\lambda$  (this being 6564.605<sub>8</sub>). For  $H_\beta$ , Paschen's wave-length is identical with Curtis's value, but, for  $H_\gamma$ , Paschen quotes  $\lambda_{\text{air}} = 4340.465$  (which is by 0.002 smaller than Curtis's value), giving  $\lambda_{\text{vac}} = 4341.681$ , and thus almost annihilating the above  $\Delta\lambda$  for  $H_\gamma$ .

Under these circumstances, the agreement of (3), (4) with observations will be found better than might be expected, especially as the six differences  $\Delta\lambda$

\* If  $H_\alpha$  is (in view of its excessive breadth) discarded from the least-square calculation, the result is  $N = 109678.07$ , differing but unessentially from the above value, and  $\sigma = +9.638 \cdot 10^{-5}$ . Curiously enough, these two coefficients give, with (3), for the main component of the excluded group  $H_\alpha$ ,  $\nu = 15233.216$ , identical in all eight figures with Curtis's value, which, of course, is a mere chance result. But these new values of  $N$ ,  $\sigma$  make the  $\Delta\lambda$  for the remaining five groups considerably greater, and, what matters more, all of the same sign (to wit, all negative).

† 'Annalen der Physik,' vol. 50, p. 935 (1916).

are irregularly distributed, and three are positive and three negative, giving  $\Sigma\Delta\lambda = 41 - 29 = 12$ , in  $10^{-4}$  Å.U., if Curtis's observed  $\lambda$  are adopted throughout. With Paschen's values for  $H_\alpha$  and  $H_\gamma$ , the agreement is, for all six groups, almost ideal.\*

Ultimately, therefore, we shall retain the values of  $N$  and  $\sigma$  given under (4). These values will be used in (3) for the main components, and in (2) for all possible components of each group of the Balmer series.

**3. Comparison with Sommerfeld's Formula.**—Before proceeding with our subject, it may be interesting to see to what extent Curtis's observations can be represented by Sommerfeld's relativistic formula, which is based on the usual assumption of a spherical nucleus ( $\sigma = 0$ ) and a variable mass of the electron. Sommerfeld himself† does not seem to have tested his formula extensively enough in this respect. It is true that he gives‡ a comparison of his theoretical values of  $\Delta N$ , the difference of the Rydberg constant in passing from  $H_\alpha$  to  $H_\beta$ , or to  $H_\gamma$ , or  $H_\delta$ , with observation. But, first of all, the "corrections" made for this purpose on the observed wave-lengths are avowedly conjectural and by no means binding; and, secondly, even if these be granted, the agreement between his theoretical figures

$$10^6 \frac{\Delta N}{N} = \begin{array}{ccc} H_\alpha - H_\beta & H_\alpha - H_\gamma & H_\alpha - H_\delta \\ 0.61 & 0.89 & 1.04 \end{array}$$

and the corrected observed ones,

$$\begin{array}{ccc} 0.37 & 0.35 & 0.06 \end{array}$$

is certainly not very reassuring. Under these circumstances, a comparison with Curtis's observations will not be out of place in our present connection.

Sommerfeld's frequency formula for the "main," *i.e.*, the circular-circular components is

$$\nu = N \left\{ \left( \frac{1}{2^2} - \frac{1}{n^2} \right) + a^2 \left( \frac{1}{2^4} - \frac{1}{n^4} \right) \right\}, \quad (S)$$

where  $a^2$  is Sommerfeld's "universal" constant (not free as our  $\sigma$ ), given by

$$a = \frac{2\pi e^2}{ch},$$

so that the coefficient of the correction term in (S) is essentially positive and, within narrow limits, fixed in its value. The value adopted by Sommerfeld, based on  $e = 4.76 \cdot 10^{-10}$ ,  $h = 6.51 \cdot 10^{-27}$ , is  $a^2 = 5.30 \cdot 10^{-5}$ .

Now, using (S) and determining  $N$  and  $a^2$ , again by the method of least squares, from Curtis's six observations, exactly as in the case of our formula (3), I find

$$N = 109677.67 \text{ and } a^2 = 3.390 \cdot 10^{-5},$$

and these coefficients, substituted in (S), give for  $\Delta\nu = \nu_{\text{calc.}} - \nu_{\text{obs.}}$  for  $H_\alpha$  up to  $H_\delta$ , the values

$$\Delta\nu = -0.020 \quad -0.012 \quad -0.005 \quad -0.009 \quad -0.014 \quad -0.022, \quad (S)$$

\* It may be argued that Mr. Curtis has represented all his six observations still better, to wit, by his formula (I), p. 148, *loc. cit.* But in this formula, which is of the Rydberg type, the two constants  $\mu = +0.0,210$  and  $p = -0.0,383$  do not seem to have an immediate physical meaning.

† 'Ann. d. Physik,' vol. 51, pp. 1-94 (1916).

‡ *Loc. cit.*, pp. 60-61.

which compare very disadvantageously with our differences corresponding to (3), (4), namely,

$$\Delta\nu = -0.009 \quad -0.001 \quad +0.007 \quad +0.006 \quad +0.004 \quad -0.002. \quad (3, 4)$$

The latter (aspherical)  $\Delta\nu$  are considerably smaller and of different signs, whereas Sommerfeld's formula gives all  $\Delta\nu$  negative. Moreover, the required value  $a^2 = 3.39 \cdot 10^{-5}$  is much too far from Sommerfeld's  $5.30 \cdot 10^{-5}$  to be admissible.\*

This, however, is by no means intended to depreciate the value of Sommerfeld's beautiful theory, which in the eyes of the present writer is one of the most admirable works in modern physics.† But the chief experimental triumphs of Sommerfeld's theory seem to lie in the fine-structure of "lines" (or groups), more especially those of Fowler's principal series of (ionised) helium. Notwithstanding these notable successes in the case of the helium lines, we must keep an open mind in judging Sommerfeld's theory with regard to our present or to any other case.

4. By what has been said in Section 2, we have good reasons for attributing to the atom of hydrogen, as far as its Balmer series is concerned, the Rydberg constant given under (4), and an *oblate* nucleus, of which the amount of asphericity is given by

$$\sigma = \left( \frac{2Nch}{e^2} \right)^2 \cdot (A-B) = +9.007 \cdot 10^{-5}. \quad (4a)$$

It may be interesting to estimate, according to this formula, the difference  $A-B$  of the principal "moments of inertia" of the hydrogen nucleus. Putting, in round figures,

$$N = 1 \cdot 10 \cdot 10^5, \quad e = 4.76 \cdot 10^{-10}, \quad h = 6.51 \cdot 10^{-27}, \quad c = 3 \cdot 10^{10},$$

$$\text{I find} \quad A-B = 2.51 \cdot 10^{-21} \text{ cm}^2. \quad (4b)$$

To form an idea of the meaning of this result, suppose the nucleus to be a homogeneous rotational ellipsoid of axes  $2a$  and  $2b$ , the former of these being the axis of symmetry. Then (*cf.*, *loc. cit.* p. 63)  $A = \frac{2}{5} b^2$ ,  $B = \frac{a^2 + b^2}{5}$ , and

$$A-B = \frac{1}{5} (b^2 - a^2),$$

so that the nucleus is oblate in the usual sense of the word. If  $\zeta$  be the eccentricity of the generating ellipse, we have  $b^2 - a^2 = b^2 \zeta^2$ , and, therefore,

\* It may be interesting to mention in this connection that a much smaller deviation from this "universal"  $a^2$ -value (to wit, 6.37 as against 5.30) has sufficed to K. Glitscher, a pupil of Prof. Sommerfeld, to condemn categorically Abraham's rigid electron in favour of Lorentz's deformable (*i.e.*, the relativistic) one. *Cf.* Glitscher's paper in 'Ann. d. Physik,' vol. 52, p. 608 (1917), or the account of it given in my 'Report on the Quantum Theory of Spectra,' London, Hilger, 1920.

† The "objections" against Sommerfeld's theory, hinted at in a footnote, p. 47 of my 'Phil. Mag.' paper (cited before), were found to be only apparent difficulties concerning the "canonical" nature of Sommerfeld's variables. This point has, in the meantime, been completely explained by Sommerfeld in a private communication to the author.

by (4b),  $b^2\zeta^2 = 5(A-B) = 1.26 \cdot 10^{-20}$ , i.e., for the product of the eccentricity into the major semi-axis of the nucleus,

$$b \zeta = 1.12 \cdot 10^{-10} \text{ cm.} \quad (4c)$$

This is, comparatively speaking, surprisingly large. For it would mean, for the equatorial semi-axis of the nucleus, at any rate,

$$b \geq 1.12 \cdot 10^{-10} \text{ cm.,}$$

the lower limit being reached for a nucleus flattened down to a disc, and, even then, its lateral dimensions would be scarcely as much as 100 times smaller than those of the whole hydrogen atom, or better, of the smallest stationary electronic orbit. Yet, the unexpectedly large value of  $A-B$  or of  $b\zeta$  does not seem to constitute a serious objection against the proposed theory. If, as is assumed by Rutherford, the mass of the nucleus is wholly electromagnetic, and its shape is spherical or almost so, then, of course, its dimensions would be of the order of  $10^{-16}$  cm. But there is certainly no evidence whatever for the purely electric nature of the nucleus (nor for its spherical form). And, although Rutherford's scattering experiments are interpreted as pointing to nucleus dimensions of the order of  $10^{-12}$  cm., or even  $10^{-13}$  cm., yet the elementary theory of Rutherford's experiments is in many instances in direct opposition to observation,\* so that the low-dimension figures often quoted after Sir Ernest Rutherford do not seem to be definitely established.

**5. Fine-Structure of  $H_\alpha$ .**—For the first member of the Balmer series, the group  $H_\alpha$ , we have to substitute in equation (2)

$$n = n_1 + n_2 + n_3 = 3,$$

so that the equation for the whole group will be

$$\frac{\nu}{N} = \frac{1}{4} \left\{ 1 + \frac{4\sigma g'}{(2-n_3')^6} \right\} - \frac{1}{9} \left\{ 1 + \frac{9\sigma g}{(3-n_3)^6} \right\}, \quad (5)$$

where, as for every group of the series,  $n' = n_1' + n_2' + n_3' = 2$ . For the main component of  $H_\alpha$  we have

$$\frac{\nu}{N} = \frac{1}{4} \left\{ 1 + \frac{\sigma}{2^4} \right\} - \frac{1}{9} \left\{ 1 + \frac{\sigma}{3^4} \right\}. \quad (5_0)$$

Let us count the frequency distance  $\delta\nu$  of any component of the group from the main component (and, similarly, their wave-length distances  $\delta\lambda$ ) Then, subtracting (5<sub>0</sub>) from (5), we shall have, for any component of the group  $H_\alpha$ ,

$$\delta\mu \equiv \frac{\delta\nu}{N\sigma} = \frac{g'}{(2-n_3')^6} - \frac{g}{(3-n_3)^6} - \frac{1}{2^6} + \frac{1}{3^6}. \quad (6)$$

\* See, for instance, 'Phil. Mag.', vol. 37, p. 553, table (1919).

The fine-structure of the whole group is thus seen to depend on  $N, \sigma$  only through their product, which, by (4) is, to three significant figures,

$$N\sigma = 9.88 \text{ cm.}^{-1}. \quad (7)$$

Since it is for the present futile to think of determining the distances of the components to within 1 per cent., we may as well take  $N\sigma = 10 \text{ cm.}^{-1}$ .

It is scarcely necessary to say that our fine-structure formula (6), and, similarly, those for  $H_\beta, H_\gamma$ , etc., are entirely different from Sommerfeld's formulæ.

Passing to the evaluation of the numerous arithmetically possible components determined by (6), it may be well to adopt a short symbol for each of them. As such we will take

$$\frac{n_1 n_2 n_3}{n_1' n_2' n_3'}$$

which will stand for the component due to the passage from the orbit  $n_1, n_2, n_3$  to  $n_1', n_2', n_3'$ . Thus the main component of the group will be  $\frac{300}{200}$ . Similarly we shall write  $\frac{210}{200}, \frac{210}{110}$ , and so on. The sum of the upper numbers will be 3, and that of the lower numbers, 2.

Notwithstanding the smallness of the totals ( $n = 3, n' = 2$ ) in the case of  $H_\alpha$ , there is still quite a multitude of components arithmetically possible. Our first task must be to reduce their number, avoiding, however, as much as possible, any arbitrary assumptions.

In the first place, since the angular momentum corresponding to any stationary orbit is\*

$$p = (n_1 + n_2) \frac{h}{2\pi},$$

and, since rectilinear orbits are not in question, we shall have to consider only such combinations of the two triads of numbers, for which

$$\left. \begin{array}{l} n_1 + n_2 > 0 \\ n_1' + n_2' > 0 \end{array} \right\}. \quad (I)$$

In the second place, it will be remembered† that the full expression for the function  $g$  appearing in our formula is

$$g = g(i, \epsilon) = 1 + \frac{3}{2}\epsilon^2 - \frac{3}{2}\sin^2 i \cdot [1 + \frac{3}{4}\epsilon^2(1 + 2\sin^2 \omega)],$$

and, since the perihelion longitude  $\omega$  is not quantisable, all components for which *both* the inclination  $i$  and the eccentricity  $\epsilon$  of the initial or the final orbit differ from zero, will be more or less *broad* bands, according to the amount of inclination and eccentricity. Now, even if such components or

\* *Loc. cit.*, p. 54.

† *Loc. cit.*, p. 55.

bands were equally probable as the remaining ones, *i.e.*, if the same numbers of individual atoms were engaged in producing them, yet, their light contributions being spaced all over the broad interval, corresponding to  $\omega = 0$  to  $2\pi$ , these bands will be much fainter than the sharp lines, in most cases, in fact, producing only a faint, hazy background to the whole group of sharp lines. At any rate, these broad components would be scarcely distinguishable, the more so as many of them overlap, as is shown by detailed calculations, which here may be omitted.

We shall, therefore, retain only *the sharp components*, *i.e.*, such only for which either  $n_2$  or  $n_3$  (or both) and at the same time either  $n_2'$  or  $n_3'$  (or both) vanish.\* We can express this restricting condition shortly by requiring

$$\left. \begin{aligned} n_2 n_3 &= 0 \\ n_2' n_3' &= 0 \end{aligned} \right\}. \quad (\text{II})$$

This will greatly reduce the number of possible arithmetical combinations. At the same time the function  $g$  will be simplified down to

$$g = 1 + \frac{3}{2}(\epsilon^2 - \sin^2 i),$$

where, by (II), either  $\epsilon$  or  $i$  (or both) vanish. Remembering that

$$\cos i = \frac{n_1}{n_1 + n_2}, \quad \epsilon^2 = 1 - \left( \frac{n_1 + n_2}{n} \right)^2,$$

we shall have, ultimately,

$$g = 1 + \frac{3}{2} \left[ \frac{n_1^2}{(n_1 + n_2)^2} - \frac{(n_1 + n_2)^2}{n^2} \right], \quad (8)$$

valid for the sharp components of any member of the series. For the group  $H_a$  we have to put here  $n = 3$ , and similarly (for  $g'$ )  $n' = 2$ .

We may subsequently consider a "selective principle," such as that given by Rubinowicz. But, in the meantime, let us consider the still numerous components left by the application of the conditions (I) and (II) alone, in short, *all sharp* components of the group  $H_a$ .

These, classified according to the final orbits (in rows, and initials in columns) are:—

$$\left. \begin{array}{cccccc} \frac{300}{200} & \frac{210}{200} & \frac{201}{200} & \frac{120}{200} & \frac{102}{200} & \frac{030}{200} \\ \frac{300}{110} & \frac{210}{110} & \frac{201}{110} & \frac{120}{110} & \frac{102}{110} & \frac{030}{110} \\ \frac{300}{101} & \frac{210}{101} & \frac{201}{101} & \frac{120}{101} & \frac{102}{101} & \frac{030}{101} \\ \frac{300}{020} & \frac{210}{020} & \frac{201}{020} & \frac{120}{020} & \frac{102}{020} & \frac{030}{020} \end{array} \right\}. \quad (9)$$

\* That is to say, orbits either equatorial or circular (or both).



The first is the main ( $\delta\nu = 0$ ). In all we have 24 components, which may be considered as four "sextets."\* The first, or the main, sextet can be shortly denoted by 2.0.0; similarly, the second by 1.1.0, and so on. A glance at equation (6) will suffice to show that all these sextets are obtainable from one another by a *rigid shift* along the scale of frequencies.† Thus it is enough to write down one of the sextets, say the first, and to indicate the rigid shifts which carry it as a whole to the position of the second, the third, and the fourth sextets.

According to (6) and (8), and since  $g(2,0,0) = 1$ , more generally  $g(n,0,0) = 1$ , the first sextet will be given by

$$\delta\mu = \frac{\delta\nu}{N\sigma} = \frac{1}{3^6} - \frac{g}{(3-n_3)^6}, \quad (2.0.0)$$

and the rigid shifts transforming this into the 2nd, 3rd, and 4th sextet will be, respectively,

$$\delta'\mu = \frac{g(1,1,0)-1}{2^6} = -\frac{9}{512}, \quad (1.1.0)$$

$$\delta'\mu = g(1,0,1) - \frac{1}{2^6} = +\frac{135}{64}, \quad (1.0.1)$$

$$\delta'\mu = \frac{g(0,2,0)-1}{2^6} = -\frac{3}{128}. \quad (0.2.0)$$

Thus, by (8) and (2.0.0), using our above value of  $N\sigma$ , passing to  $\delta\lambda = -\lambda^2\delta\nu$ , and ordering the components after their increasing wave-length, we have, in Å.U., for the first sextet

$$\begin{array}{cccccc} 0.3.0. & 1.2.0. & 2.1.0. & 3.0.0. & 2.0.1. & 1.0.2. \\ \delta\lambda = -0.0088 & -0.0078 & -0.0049 & 0 & 0.1163 & [+9.9289], \end{array} \quad (2.0.0)$$

and for the shifts carrying this sextet rigidly into the remaining three sextets, according to the last quoted values of  $\delta'\mu$ ,

$$\delta'\lambda_{(0.2.0)} = +0.0998; \quad \delta'\lambda_{(1.1.0)} = +0.0748; \quad [\delta'\lambda_{(1.0.1)} = -8.9812].$$

Let us discard, for the present, the very eccentric, and therefore distant, component of (2.0.0), and the corresponding components of (0.2.0), (1.1.0), as well as the whole distant sextet (1.0.1), distinguished by square brackets. Moreover, in view of the actual limits of spectroscopic precision, let us retain but the third decimals of Å.U. Then the whole material can be written as follows (regardless of the provisional grouping into "sextets," which are now partly intermingled):—

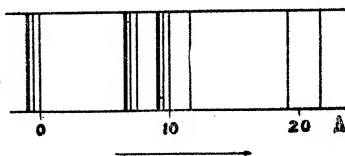
\* If the reader prefers to classify them according to the initial orbits, he can consider the whole group, with equal right, as consisting of *six quartets*.

† At the same time we have six quartets, 3.0.0, 2.1.0, etc., following from one another by other rigid shifts.

Fine-Structure of  $H_\alpha$ .

Component.	$\delta\lambda$ in $\text{\AA.U.}$
030	-0.009
200	
120	
200	-0.008
210	
200	-0.005
300	
200	
030	0.000
110	+0.066
120	
110	
210	0.067
110	
300	0.070
110	
030	0.075
020	
120	
020	0.091
210	
020	0.092
300	
020	0.095
201	
200	0.100
201	
110	0.116
201	0.191
110	
201	0.216
020	

These are in all 15 components, of which those joined by brackets are so close together as to be scarcely separable from one another by available spectroscopic means. As such they are drawn on the accompanying figure.



We may now consider A. Rubinowicz's selective principle ("Auswahlprinzip"),\* mentioned before. This requires "the azimuthal quantum number of an atom to jump at the utmost by a unit"; that number is in our (three-

\* 'Physik. Zeitschrift,' vol. 19, pp. 441, 465. See also Chap. VI of Sommerfeld's book, just published, 'Atombau und Spektrallinien,' Brunswick, 1919.

dimensional) case  $n_1 + n_2$ , the factor of  $h/2\pi$  in the value of the angular momentum, so that Rubinowicz's selective principle means

$$(n_1 + n_2) - (n_1' + n_2') = +1 \text{ or } -1 \text{ or } 0. \quad (\text{Rub.})$$

Now, although we have made no use of this well-founded principle in drawing up our list, it so happens that all the 15 components satisfy it, as a glance at the first column of the list will show.\* The more advisable does it seem to retain, for the present at least, all these 15 sharp components of the  $H_\alpha$  group. We may have to discard some of them on the evidence of further more precise measurements, which, as I learn from Dr. Merton, are now contemplated by him jointly with Prof. Nicholson.

For the present, little more can be said than that the above fine-structure is not contradicted by the available observations on  $H_\alpha$ . In fact, what up to the present is known of this group is that it is separable into two conspicuous "components," 0.132 Å.U. apart,† the stronger component being the more red one. Now, in a first approximation (and especially in view of the light background due to the discarded broad components or bands) our first four theoretical components, together with the main which they so closely accompany, can be interpreted as the less red, and all the remaining, fused together, as the second, more red "component." The "centre" of the former can be taken to lie at  $\delta\lambda = -0.005$ , and that of the latter somewhere between 0.13 and 0.14, and this would give, roughly, the observed "separation of the two components," correct at least as to its order of magnitude. I understand from Dr. Merton's private communications that  $H_\alpha$  is very likely to have a much more complicated structure than that usually described by a "doublet," a third component, in fact, appearing, under certain circumstances, between the two others. Also a suggestion made by Prof. Fowler would make it likely for  $H_\alpha$  to be a typical triplet,‡ and this would answer better our configuration of components, in which there are two comparatively large gaps, one between 0 and 0.066, and another between 0.116 and 0.191. But a final verdict must be postponed until more precise experimental results are available. We will leave, therefore, for the present any further discussion of the fine-structure of the  $H_\alpha$  group.

\* Bohr's sharpened form of the selective principle excludes the *zero*, and thus would exclude our last three components. But, although certain cases speak for Bohr's principle, there are certainly no reasons for universalizing it.

† Buisson and Fabry, recently confirmed by Merton and Nicholson ('Phil. Trans,' vol. 217, p. 275 (1917)), who find from 0.130 to 0.134 with a mean of 0.1323.

‡ Cf. Merton and Nicholson, *loc. cit.*, p. 262.

6. *Fine-structure of  $H_\beta$ .*—The equation of this group is, analogously to (6),

$$\frac{\delta\nu}{N\sigma} = \frac{g'}{(2-n_3')^6} - \frac{g}{(4-n^3)^6} - \frac{1}{2^6} + \frac{1}{4^6}, \quad (10)$$

with  $n = n_1 + n_2 + n_3 = 4$ . The final orbits will be as before. The initial ones will, of course, be more numerous. Classifying, again, all the components, which satisfy (I) and (II), according to the final orbits, we shall now have the octet 2.0.0,

$$\begin{array}{cccccccc} \frac{400}{200} & \frac{310}{200} & \frac{301}{200} & \frac{220}{200} & \frac{202}{200} & \frac{130}{200} & \frac{103}{200} & \frac{040}{200} \end{array}$$

and three more octets, 1.1.0, 1.0.1, 0.2.0, obtainable from this by the same rigid shifts as in the case of  $H_\alpha$ . The whole group  $H_\beta$  would thus consist of 32 sharp components. Discarding, again, the very eccentric, and therefore very distant components, and proceeding in much the same way as before, we should still have as many as 21 components, whose  $\delta\lambda$  range from  $-0.0009$  to  $+0.1335$  Å. Of these, however, unlike the previous case, the greater part infringes against Rubinowicz's selective principle. Discarding all these, to which belongs also the main itself  $\frac{400}{200}$ , the components  $\frac{040}{200}$ ,  $\frac{040}{110}$  and 12 others, we are left with only six sharp components satisfying Rubinowicz's principle, to wit,

$$\begin{array}{cccccc} \frac{301}{200} & \frac{301}{110} & \frac{301}{020} & \frac{202}{200} & \frac{202}{110} & \frac{202}{020} \\ \delta\lambda = +0.004_6 & 0.045_6 & \underline{0.059_4} & 0.078_7 & 0.119_8 & \underline{0.133_5} \text{ Å.} \end{array} \quad (H_\beta)$$

According to Bohr's rule,\* one would still have to discard the two underlined components. But, in view of the incomplete experimental knowledge of the structure of this group, it will be best to leave the matter here for the present.

For the same reason it will be better to postpone also a desirable and possible retouching of the coefficients (4), and especially of  $N$ , in view of the manifestly *acentral* position of the main component within the theoretical group  $H_\alpha$  as well as  $H_\beta$ , and presumably also  $H_\gamma$ , etc. Such a redetermination of  $N$ ,  $\sigma$  might still improve the already good agreement of (3), (4) with Curtis's measurements.

\* Which "prohibits" all combinations with  $n_1 = 0$  or  $n_1' = 0$ . Cf. Sommerfeld's 'Atombau,' etc., p. 451.